

**EFFECT OF LEAD-FREE SOLDER AND GOLD CONTENT ON THE SHEAR
STRENGTH, TOUGHNESS, IMC AND VOID FORMATION**

By

OO CHENG EE

**Thesis submitted in fulfilment of the
requirement for degree
of Master of science**

May 2004

ACKNOWLEDGEMENT

Firstly, I would like to thank my project supervisor, Dr. Azizan Aziz and co-supervisor, Dr. Luay Bakir Hussain for their guidance, advice and help throughout the whole research project.

Besides that, I would like to thank my site supervisor OP Lim for his full support in getting the project done.

Not forgetting to thank the school of Material Engineering for allowing me to do research with the faculty in order my for knowledge and career enhancement. The many chances given to me to present in front of postgraduates students and gather inputs and insights from them is highly appreciated.

Besides, I would like to express my sincere thanks to Peter Collins representing Commercial Department of National Physical Laboratory (NPL), United Kingdom in granting the permission to use the chart on Gold Embrittlement Prevention Guideline (Figure 2.4) by NPL in this master report.

Last but not least, thanks to all others directly or indirectly helping up with the project to make the project a success.

CONTENTS

1.0 ACKNOWLEDGEMENT

ii

Formatted: Bullets and Numbering

CONTENTS

iii

LIST OF FIGURES

vii

LIST OF TABLES

x

LIST OF ABBREVIATIONS

xi

ABSTRACT

xii

ABSTRAK

xiii

CHAPTER 1: INTRODUCTION

Introduction

1

1.1 Objectives

4

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

5

2.2 Lead Free Alternatives

5

2.3 Effect of tin-lead (~~Pb~~) to solder system

~~-109~~

~~2.4~~ 2.3.1 Adverse Effects of Lead (Pb)

Formatted: Bullets and Numbering

~~140~~

2.3.2 Adverse Effects of Tin (Sn)

12

2.5 2.4 Solder Characteristic	13
Effect of Tin (Sn) to solder system	
12	
2.6Solder Characteristic	13
2.46.1 Melting Temperature	13
2.46.2 Microstructure	14
2.46.3 Intermetallic Compound (IMC)	14
2.4.6.4 Mechanical Properties	15
2.64.4.1 Time-Independent Monotonic Deformation	16
2.46.4.2 Time Dependent Monotonic Deformation	16
2.46.4.3 Cyclic Deformation or Fatigue	17
2.7 2.5 Why Gold is used	18
2.82.6 Thick Gold versus Thin Gold	
19Gold in Semiconductors and Microelectronics	
18	
2.9 Thick Gold versus Thin Gold	19
2.10 2.7 Gold Solder Embrittlement Issue	
20	
2.11 2.8 AuSn Intermetallic	
23	
2.12 2.9 AuSn Intermetallic Failure Mechanism	
25	

Formatted: Bullets and Numbering

Formatted: Bullets and Numbering

2.13 <u>2.10</u> Gold Interaction with Lead Free Solders	
26	
2.14 <u>2.11</u> General Guideline to prevent gold embrittlement	
28	
2.15 <u>2.12</u> Kinkendall Effect	
30	
2.16 <u>2.13</u> Design of Experiment	
32	
2.1 63 <u>3</u> .1 Design Type	34
2.1 63 <u>3</u> .2 ANOVA (Analysis of Variance)	
35	
2.17 <u>2.14</u> Shear Test	
42	

← - - - Formatted: Bullets and Numbering

CHAPTER 3: METHODOLOGY

3.1 Introduction	46
3.2 List of equipment	46
3.3 Materials	46
3.4 Experiment Procedure	47
3.4.1 Design of Experiment (DOE)	48
3.4.1.1 Assumption	49
3.4.2 Material Preparation	52
3.4.3 Experiment Processes/Testing/SEM/EDX	53

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1	Introduction	58
4.2	DOE Result Analysis	59
4.3	Optical Microscopy Characterization	69
4.4	Destructive Test Analysis	71
4.5	Toughness Analysis	72
4.6	Destructive Shear Fracture Surface Analysis	77
4.7	X-Ray Analysis	80
4.8	SEM/EDX Characterization	83

CHAPTER 5: CONCLUSION

5.1	Effect of Au wt% on lead free (SAC) and lead (SnPb)	89
5.2	IMC, Void and Toughness Relationship	89
5.3	Viability of SAC as replacement for SnPb on thick gold application	89
5.4	Recommendation on implementation guideline	90

CHAPTER 6: SUGGESTIONS

REFERENCES

BIBLIOGRAPHYGENERAL REFERENCES

99

APPENDICES

	APPENDIX A
10	16
	APPENDIX B
10	38
	APPENDIX C
10	54
	APPENDIX D
10	74
	APPENDIX E
10	94
	APPENDIX F
11	27
	APPENDIX G
11	38
	APPENDIX H
11	62
	APPENDIX I
11	72
	APPENDIX J
11	82

LIST OF FIGURES

		Pages
Figure 1.1	A schematic to show groundwater lead pollution due to landfills of scrapped electronics components	1
Figure 2.1	Dissolution rates at various temperatures for a number of metals in 60% Sn 40% Pb solder	21
Figure 2.2	(a) <i>Top</i> : Influence of Gold content in 63% tin-37% lead solder on tensile strength ductility (b) <i>Middle</i> : Diamond hardness of 63% tin-37% lead solder for various gold contents (c) <i>Bottom</i> : Effect on impact strength of 63% tin-37% lead solder of increasing concentration of gold	22
Figure 2.3	Phase Diagram of Au and Sn	24
Figure 2.4	Gold Embrittlement Prevention Guideline	29
Figure 2.5	Schematic representative of Kirkendall void formation with presence of gold on solder	31
Figure 2.6	DOE result plots	41
Figure 2.7	Six different modes of ball shear failure	43
Figure 2.8	Solder Ball Shear Tool Setup	44
Figure 2.9	Stress-Strain Curve	45
Figure 2.10	Stress-Strain Curve comparing strong and tough	45
Figure 3.1	Solder pad pattern	52
Figure 3.2	(a) Ribbon Tacking, i.e. 12 mil (b) Solder Dispensing	55 55
Figure 3.3	Reflow Profile for (a) Lead SnPb (b) Lead Free (SAC)	55 55

Figure 3.4	X-ray showing (a) Incomplete dissolution of Au (b) Complete dissolution	56 56
Figure 3.5	DAGE 2400A Shear Tester	56
Figure 3.6	Shearing Method	57
Figure 3.7	Example shear displacement measurement (a) Shear displacement top view (b) Shear displacement side view	57
Figure 4.1	DOE result plot for (a) Lead Free Solder (b) Lead Solder	59 60
Figure 4.2	Interaction Plot for (a) Lead Free Solder (b) Lead Solder	61 61
Figure 4.3	Effect of Au wt% on surface morphology change For (a) Lead Free Solder (b) Lead Solder	70
Figure 4.4	Destructive Shear Force for comparison of lead and lead free solder at 10wt % Au	71
Figure 4.5	Shear-Displacement curves for (a) Lead free SAC and (b) Lead SnPb	73 74
Figure 4.6	Toughness Comparison of lead and lead free solder at various Au wt%.	75
Figure 4.7	Destructive shear fracture surface for Lead SnPb (50x) at (a) 0% Au (b) 2.5% (c) 5% (d) 10%	77
Figure 4.8	Destructive shear fracture surface for Lead Free SAC (50x) at (a) 0% Au (b) 2.5% (c) 5% (d) 10%	78
Figure 4.9	X-ray pictures for lead solder SnPb (40x) at (a) 0% Au (b) 2.5% (c) 5% (d) 10%	80
Figure 4.10	X-ray pictures for lead free solder SAC (40x) at (a) 0% Au (b) 2.5% (c) 5% (d) 10%	81

Figure 4.11	(a) SEM photo on lead free solder ball (0% Au)	84
	(b) SEM photo on lead free solder ball (2.5% Au)	84
	(c) SEM photo on lead free solder ball (5.0% Au)	85
	(d) SEM photo on lead free solder ball (10% Au)	85
Figure 4.12	(a) SEM photo on lead solder ball (0% Au)	86
	(b) SEM photo on lead solder ball (2.5% Au)	86
	(c) SEM photo on lead solder ball (5.0% Au)	87
	(d) SEM photo on lead solder ball (10% Au)	87
Figure 4.13	EDX analysis of SAC showing AuSn detected at interface <u>pointed</u> <u>areas of Figure 4.11</u>	
	88	
Figure 4.14	EDX analysis of SnPb showing AuSn detected at interface <u>detected at</u> <u>pointed</u> <u>areas of Figure 4.11</u>	88
Figure 5.1	Chart showing recommended gold embrittlement guideline for SAC solder	91

LIST OF TABLES

	Pages
Table 2.1 Alloy Impact on Solder Performance	56
Table 2.2 Comparison of Candidate Elements	67
Table 2.3 List of candidate lead free solders	78
Table 2.4 Solder Properties	89
Table 2.5 Type of Errors	36
Table 3.1 DOE Plan	48
Table 3.2 Sample Board Details	52
Table 3.3 Shear Test Setup Parameters	54

LIST OF ABBREVIATIONS

BGA	-	Ball Grid Array
CSP	-	Chip Scale Package
IMC	-	Intermetallic Compound
IPC	-	Association Connecting Electronics Industries
JEDEC	-	Joint Electronic Device Engineering Industry Development
JEIDA	-	Japanese Electronic Industry Development Association
NEMI	-	National Electronics Manufacturing Initiatives
NIST	-	National Institute of Standards and Technology
NPL	-	National Physical Laboratory, UK
PBGA	-	Plastic Ball Grid Array
RoHS	-	Restriction of Hazardous Substances
SAC	-	SnAgCu (Tin/Silver/Copper)
SEM	-	Scanning Electron Microscope
WEEE	-	Waste Electronics and Electrical Equipment

ABSTRACT

Study of interaction between lead free solder with gold and the mechanical toughness, shear strength of solder that associated with intermetallic compound IMC and void formation was carried out. Eutectic tin-lead solder is used as a control for the experiment. Effect of IMC formation to joint reliability is studied by varying the gold concentration from 0 to 10wt%. A rough guide of implementation to prevent gold embrittlement to Sn3.8Ag0.7Cu (SAC) is given at the end of the research. Lead free solder that included in the study is Sn3.8Ag0.7Cu (SAC) with 63Sn37Pb as control and surface finishes studied are Au on copper substrate. Physical analysis equipment SEM/EDX, X-ray and high power optical scope for IMC microstructure investigation are utilized. For Shear Test analysis, DAGE 2400A instrument was used. It is found out in this study that lead free Sn3.8Ag0.7Cu SAC solder is not a good replacement for eutectic tin-lead solder when gold wt% increases above 2.5 wt%. Evidently as the formation of IMC increased combined with the formation of voids, the solder joint toughness was decreased.

**KESAN LOGAM PATERI TANPA PLUMBUM DAN KANDUNGAN EMAS KE
ATAS KEKUATAN RICIH PATERI, KELIATAN, PEMBENTUKAN
KOMPAN ANTARALOGAM DAN LOMPON**

ABSTRAK

Kajian tentang interaksi antara logam pateri tanpa plumbum dengan emas dan keliatan, kekuatan ricih yang berkait rapat dengan pembentukan kompaun antaralogam dan lompong. Eutetik tin-plumblum pateri digunakan sebagai kawalan dalam eksperimen ini. Kesan pembentukan antaralogam terhadap reliabilitas (kebolehpercayaan) ikatan pateri dikaji dengan mengubah kepekatan kandungan emas dari 0% hingga 10 %. Satu panduan tentang aplikasi bagi mengelakkan kesan kerapuhan diberi pada akhir kajian. Logam pateri tanpa plumbum yang dikaji ialah Tin/3.8Perak/0.7Kuprum (SAC) dan 63Tin37Plumblum sebagai kawalan dan permukaan yang dikaji ialah emas atas kuprum. Alatan analisis fizik yang digunakan termasuk SEM/EDX, sinar-X, mikroskop optik berkuasa tinggi untuk kajian mikrostruktur antaralogam dan DAGE 2400A untuk penguji ricih. Kajian ini mendapati bahawa SAC bukan pengganti yang baik untuk eutetik tin-plumbum pateri apabila kandungan emas mencapai 2.5%. Selain itu, terdapat bukti yang jelas bahawa keliatan merosot dengan pertambahan pembentukan antaralogam dan lompong.

CHAPTER 1

INTRODUCTION

Solder is a eutectic glue to hold electronic components together. Unfortunately it is also toxic due to its lead content. In United States of American, lead ban in paint had been enacted in 1978 after lead poisoning issue (CPSC, 1977). Today the world's trend, especially in Japan and Europe, is towards a lead ban for electronics interconnect as a result of the worry of ground water contamination due to lead oxide leaching from the land-filled scrapped PCBs or other lead containing electronics components as shown in Figure 1.1 below.

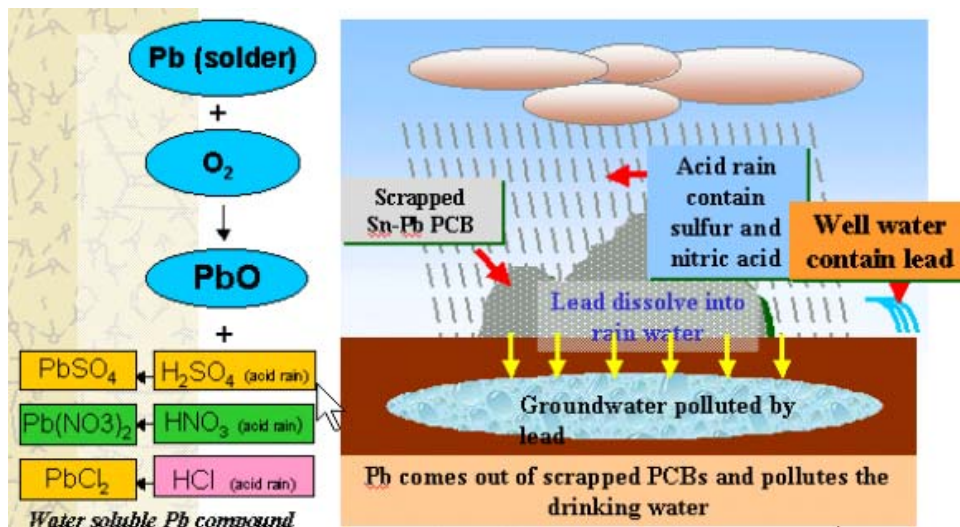


Figure 1.1: A schematic to show groundwater lead pollution due to landfills of scrapped electronics components (Lau (1), 2003)

Lead is known to have adverse health effects when it accumulates in the body over time. Lead binds strongly to proteins in the body and inhibits normal processing and functions. Nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, as well as reduced production of hemoglobin resulting in anemia and hypertension are some of the adverse effects of lead on human health. When the level of lead in the blood exceeds 40ug/100g of blood, lead poisoning is considered to have occurred (Ng, 2002). A lead level even well below the established official threshold can be hazardous to a child's neurological and physical development.

The concern about the use of lead in the electronics industry stems from occupational exposure, lead waste derived from the manufacturing process and the disposal of electronics assemblies. Therefore, US Environmental Protection Agency (EPA) has cited lead and its compounds as one of the top 17 chemicals that pose the greatest threat to human life and the environment (Mulugeta and Guna, 1998)

~~This has forced the NEMI (National Electronics Manufacturing Initiatives) taskforce to work hard towards meeting the ban of lead in electronics application by 1st July, 2006 as approved by Europe RoHS (Restriction of Hazardous Substances). Their primary emphasis is on Sn/Ag/Cu (SAC) as “one single solution” for lead replacement (Galen, 2003).~~

However, some people argue that less than 2% of the production of lead worldwide (John, 2003) is used in solders for the electronic industry. Therefore the worry about

amount of lead from printed circuit board go into landfill may leach into ground water and endanger marine life is unconvincing for the need of lead ban.

The lead-free debate is no longer about the environmental impact or about technical issues. It is more to a marketing issue following the success story of Panasonic Japan in securing an estimated of 11% of market share available after the introduction of lead-free portable mini-disc player (MiniDisc MJ30) as a green product in October 1998 (John, 2003).

~~Despite the argument,~~ The fact is that the decision of Japanese companies to go lead-free is forcing the US and Europe to take decision now. Big US companies are following the main stream now example Intel, the chip giant recently announced its move to remove all but five per cent of the lead it currently uses to construct processors and chipsets (Tony, 2004).

~~The lead free debate is no longer about the environmental impact or about technical issues. In the meantime, it is more to a MARKETING issue following the success story of Panasonic Japan share increment from 4.7% to 15% after the introduction of lead-free portable mini-disc player (MiniDisc MJ30) as a green product in October 1998. Besides, Toshiba has developed lead-free solders suitable for high-density cellular phones. Nortel Networks has produced lead-free Meridian phones at four different sites in North America and Europe [1].~~

In short, manufacturers who jump on the lead-free bandwagon now will have the market advantage—the sooner the better.

This had forced the NEMI (National Electronics Manufacturing Initiatives) taskforce to work hard towards meeting the ban of lead in electronics application by 1st July, 2006 as approved by Europe RoHS (Restriction of Hazardous Substances). Their primary emphasis is on Sn/Ag/Cu (SAC) as “one single solution” for lead replacement (Galen, 2003).

However, there are technological issues need to be addressed following the conversion, mainly about the higher melting point of the lead free solder, tighter process window, potential damage to heat sensitive components, surface finish incompatibility and the long-exist gold (Au) embrittlement issue that is concerned to be exaggerated by new lead free solder SAC especially for thick gold coating (3-5 μm) application in some industries e.g. microwave and radio frequency industries. However, there are still lacking in literatures about the interaction of lead free solder e.g. SAC with gold, especially thick gold. It is interesting to study if the long known gold embrittlement issue with existing eutectic tin-lead solder will exist for SAC lead free solder as well and to what extend. The research in this area is important as a fundamental knowledge for future implementation.

1.1 Objectives

The objectives of the project being run are as follows:

- i) To study the effect of Au wt% on lead free (SAC) and lead (SnPb) solder joint characteristic in terms of shear strength, toughness, IMC and void formation

- ii) To study the correlation between IMC with void formation and associated toughness
- iii) To assess the viability of lead free solder (SAC) as a replacement for existing eutectic lead solder on thick gold application
- iv) To establish guideline to avoid gold embrittlement of SAC solder

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Solder has long been a popular conductive glue to hold electronic components together especially eutectic 63Sn37Pb solder. Unfortunately it is also known for its toxicity due to its lead content. Today, ~~the world's trend, especially especially in Japanese~~ and

Europe is moving towards a lead ban for electronics interconnect as a result of the worry of ground water lead contamination due to lead oxide leaching and also occupational lead health and safety concern. This together with economic pressure has driven the development works in recent decades to work out the lead free solder replacement.

2.2 Lead Free Alternatives

Lead free by definition is the electronic products which none of their components or raw materials contains Lead (Pb) that is intentionally added, or contain more than 0.1% of incidental Pb impurities by weight. Today there is still no common world standard for stipulation of lead content as impurities to lead free solders, however JEIDA defined it as 0.1 weight % while JEDEC defined it as 0.2 weight % (Lau (1), 2003). There are list of lead free solders available in the markets however for the most economical and technological means, SAC is always recommended.

Table 2.1 and 2.2 below show some candidates elements for selection in regards to its impact to solder property, relative cost, toxicity and resource availability. In lieu of SnPb eutectic, all viable lead-free solder cannot run away from being Sn-based system (i.e., a minimum of 60 weight % of tin). This was concluded based on fundamental materials science and practical perspectives (Hwang, 2001). Fundamentals include metallurgical bonding capability on commonly used substrates, wetting ability during reflow process, and metallurgical interactions or alloying phenomena between elements. Practical factors include the availability of natural resources, manufacturability, toxicity

and cost. In summary, the criteria for lead free solder are non-toxic, available and affordable, narrow plastic range, acceptable wetting, manufacturable material, acceptable processing temperature and can form reliable joint.

Table 2.1: Alloy Impact on Solder Performance (Ng, 2003)

Property	Lead (Pb)	Silver (Ag)	Antimony (Sb)	Bismuth (Bi)	Copper (Cu)
Melting Point	X	X	X	X	X
Better wetting		X			
Increase mechanical strength		X	X		
Reduce metal dissolution		X			x
Cost reduction	X				
Corrosion Resistance			X		

Table 2.2: Comparison of Candidate Elements (Michael, 2000)

Element	Effect	Relative Cost	Toxicity	Resource Availability (Relative World production per annum in 1000 tonne)
Pb	Low eutetic (increases mechanical strength of tin)	1 (US\$488/tonne in 11/1998)	High (Carcinogen and teratogen)	1 (2800)
Sn	Too much tin causing tin whiskers	12	Moderate-low	0.07
Cu	Too much copper causing long term embrittlement	3	High	3.8
Ag	Decrease			

	melting point	327	High (Inhale)	0.005
Zn	Extremely fast oxidation	2	Minimal	2.6
Bi	Decrease melting point, increase brittleness	15	Moderate	0.001
Sb	Increase strength and brittleness	3	High (Oral)	0.035
In	Decrease melting point	564	High	0.00006

It can be seen from Table 2.2 above that with lead (Pb) as the reference, all other candidates can be proven to be relatively more expensive, especially silver (Ag) (327x) and Indium (In) (564x) due to the relatively scarce supply of the world (0.005 and 0.00006 tonnes per annum respectively). However, Pb appeared to be most toxic. Zinc (Zn) with relatively lowest price and plenty of world supply compared to other candidates is not chosen in most case due to its extremely fast oxidation. In the contrary, despite its high price, silver-Ag is selected in most cases due to its ability to reduce melting point, reduce metal dissolution and increase mechanical strength (Table 2.1). Example list of lead free solders can be seen from Table 2.3 below.

Table 2.3: List of candidate lead free solders (Michael, 2000)

Alloy category	Composition	Solidus (°C)	Liquidus (°C)	Note	Density	Advantages	Disadvantages
Sn-Pb	63Sn-37Pb	183	183	Eutectic	8.4	Overall good properties, low cost	Structural coarsening; prone to creep
Au-Sn	80Au-20Sn	280	280	Eutectic	14.51	Creep and corrosion resistant	Hard and brittle; melting point too high; expensive
Bi-Cd	60Bi-40Cd	144	144	Eutectic	9.31	Low mp	Toxic
Bi-In	67Bi-33In	109	109	Eutectic	8.81	Low mp	Poor wetting on Cu
Bi-Sn	58Bi-42Sn	138	138	Eutectic	8.56	Good fluidity	Strain rate sensitivity; poor

							wetting
In-Ag	97In-3Ag	143	143	Eutectic	7.38	Low mp	Poor wetting; expensive
In-Ag	90In-10Ag	141	237		7.54	Low mp	Poor wetting; expensive
In-Bi-Sn	51.0In-32.5Bi-16.5Sn	60	60	Eutectic	7.88	Low mp	Poor wetting; expensive
In-Sn	60In-40Sn	118	~127			Low mp	Poor wetting; expensive
In-Sn	52In-48Sn	118	118	Eutectic	7.3	Low mp	Poor wetting; expensive
In-Sn	50In-50Sn	118	125		7.3	Au soldering	Mp too low; poor fatigue and mechanical properties; expensive
Sn	100Sn	232	232		7.28	Ease of plating	Tin whisker
Sn-Ag	96.5Sn-3.5Ag	221	221	Eutectic	7.36	Wetting	Whisker and tin pest growth
Sn-Ag-Cu	93.6Sn-4.7Ag-1.7Cu	216	216	Eutectic	7.5	No coarsening	High mp
Sn-Ag-Cu	96.5Sn3.8Ag0.7Cu	217	217	Eutectic	7.50	Creep	Higher mp
Sn-In	58Sn-42In	118	145		7.3	Low mp	Poor creep
Sn-In-Ag	77.2Sn-20.0In-2.8Ag	175	187		7.25	Low mp	Expensive
Sn-Zn	91Sn-9Zn	199	199	Eutectic	7.27	Good strength; abundant	Poor corrosion resistance and wetting; high drossing

In terms of alloy selection from Table 2.3, alloy Sn-Ag-Cu with eutectic melting point at 217 °C and good creep strength is generally selected despite its higher melting point. It can be seen from Table 2.3 also that 77.2 Sn/20In/2.8Ag melting point is very close to eutectic Sn/Pb solder, however it is not a popular alloy and not been considered due to its high cost as a result of the In content. Besides, it forms a low temperature eutectic phase In/Sn around 112 – 118 °C which is very bad for a solder joint. It normally used

if thermo-cycling or end use requirements do not exceed 100 °C. Other lead free solder candidates like AuSn is normally used for high temperature application which melting point is high at 280 °C and this solder is expensive due to gold-Au content (80%).

Table 2.4 is some comparison of SAC and SnPb solders properties obtained from NIST 2002 online database. In comparison to eutectic SnPb, SAC with higher melting point of 217 °C has lower density, however better electrical, thermal conductivity and creep strength as depicted by Table 2.4 below. Sn-Ag-Cu is almost comparable to SnPb solder in terms of its properties, in fact in certain aspect like creep strength, it is better than eutectic Sn/Pb solder.

Table 2.4 (NIST, 2002)

Solder Type	Melting Point (°C)	Density (g/cm ³)	Coefficient of Thermal Expansion (ppm/°C)	Electrical Conductivity (% IACS)	Electrical Resistivity, $\mu\Omega\cdot\text{cm}$	Thermal Conductivity (W/mK)	Brinell Hardness (HB)	Creep Strength, N/mm ² at 0.1 mm/min
Sn/Pb	183	8.4	21.4 @ 25 °C	11.90	14.5	57.9 @ 32.6 °C	17	3.3 (20 °C) 1.0 (100 °C)
95.5Sn/ 3.8Ag/0.7Cu	217	7.5	22 @ 25 °C	13.00	13.0	82.0 @ 23.9 °C	15	13.0 (20 °C) 5.0 (100 °C)

#100 %IACS = 58.00 MS/m

2.3 Effect of tin-lead (~~Pb~~) on solder system

Formatted

2.3.1 Effect of Lead (Pb)

Formatted

Since the work is to get rid of lead, it is important to know what the lead actually does that makes it such a good choice for years after years of solder application. By appearance, lead is a bluish-gray metal with a bright metallic luster when the surface is

freshly exposed. In ordinary air, the surface deteriorates rapidly, taking on the dull gray appearance. This tarnish is very tenacious and protects the metallic surface from further environmental attack, which is why lead were preserved for thousand so years in the ground or other relative corrosive environment. Lead is very soft metal with great ductility and can be easily formed. It can form eutectic alloy with tin with melting point at 183 °C, low enough for most industries application.

As one of the primary components of eutectic solders, lead imparts many technical advantages to tin-lead solders (Mulugeta and Guna, 1998), including the following:

- It reduces the surface tension of pure tin and the lower surface tension of solder which facilitates wetting (Vianco, 1993)
- As an impurity in tin at levels as low as 0.1%, lead prevents the transformation of white or beta tin to gray or alpha tin upon cooling (see more explanation for such transformation in section 2.5). The reaction results in a 26% increase in volume, and the transformation causes loss of structural integrity to the tin. (Vianco, 1993)
- Pb serves as a solvent metal to enable other joint constituents, such as Sn and Cu, to rapidly form intermetallic bonds.

These factors, combined with lead being a readily available and low cost metal, make it an ideal alloying element with tin.

However, despite the advantages, it's also well substantiated that the common thermal fatigue failure for solder interconnects is linked with the Pb-rich phase. Because of

limited solubility and precipitation, Sn solute atoms cannot effectively strengthen the Pb-rich phase. At room temperature, the limited solubility of Pb in Sn matrix renders it incapable of improving the plastic deformation slip. Under temperature cycling (thermomechanical fatigue) condition, this Pb-rich phase tends to coarsen and eventually, lead to a solder joint crack (Hwang, 2001). It's therefore hopeful that the new lead free solder alternative developed with absence of Pb can impart an improved mechanical behavior.

Meanwhile, it is likely that industry may be increasingly required to recycle lead. The use of recycled lead for electronics applications, however, can be severely limited since recycled lead emits alpha particles, which can have detrimental effects on the performance of integrated circuits (Mulugeta and Guna, 1998).

Today, the world is still lacking comprehensive data about the lead free solder compared to lead system. The lead based systems have relatively well-established knowledge base about their physical metallurgy, mechanical properties, flux chemistries, manufacturing processes and reliability of eutectic tin-lead solders. Soldering on lead free solder is still a risk and need special attention (Mulugeta and Guna, 1998).

2.3.2 Effect of Tin (Sn)

2.4 Adverse Effects of Lead

2.5

Formatted

Formatted: Bullets and Numbering

Formatted

Formatted

~~2.6 When lead accumulates in the body over time, it can have adverse health effects. Lead binds strongly to proteins in the body and inhibits normal processing and functions. Nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, as well as reduced production of hemoglobin resulting in anemia and hypertension are some of the adverse effects of lead on human health.~~

~~2.7~~

~~2.8 When the level of lead in the blood exceeds 40ug/100g of blood, lead poisoning is considered to have occurred (Ng, 2002). A lead level even well below the established official threshold can be hazardous to a child's neurological and physical development.~~

~~2.9~~

~~2.10 The concern about the use of lead in the electronics industry stems from occupational exposure, lead waste derived from the manufacturing process and the disposal of electronics assemblies.~~

~~2.11~~

~~2.12 Therefore, US Environmental Protection Agency (EPA) has cited lead and its compounds as one of the top 17 chemicals that pose the greatest threat to human life and the environment (Mulugeta and Guna, 1998)~~

~~2.13~~

~~2.14~~

~~2.15~~

~~2.16~~

~~2.17~~

~~2.18 Effect of Tin (Sn) on solder system~~

Formatted: Bullets and Numbering

Because of its ability to wet and spread on a wide range of substrates using mild fluxes, tin has become the principal component of most solder alloys used for electronic applications. Tin exists in two different forms with two different crystal structures. White or β tin has a body centered tetragonal crystal structure and is stable at room temperature. Gray tin or α tin, which has a diamond cubic crystal structure, is thermodynamically stable below 13°C . The transformation of β to α tin, also called "tin pest," takes place when the temperature falls below 13°C , and results in a large increase in volume that can induce cracking in the tin structure. Consequently, tin pest can be a problem for applications that operate at temperature below 13°C .

Tin is also prone to whisker growth. Whiskers can be defined as a spontaneous columnar or cylindrical filament, which rarely branches, of mono-crystalline tin emanating from the surface of a plating finish. (Irina, 2003). Tin whiskers are tetragonal β -tin that may grow in response to internal stress in the material or external loads (Lau (2), 2003). Rapid whisker growth in tin occurs at about 51°C and is influenced by plating conditions and substrate property. Whiskers do not affect solderability nor do they cause deterioration of the tin coatings. However, longer whiskers may cause electrical shorts in PC board assemblies. Elements such as lead suppress whisker growth in tin, and virtually no whisker growth is encountered in eutectic tin-lead solder (Mulugeta & Guna, 1998).

2.192.4 Solder Characteristic

Formatted: Bullets and Numbering

Soldering is a well-known metallurgical joining method using a filler metal (the solder) with a melting point below 425°C. In order to form a proper metallurgical bond between two metals, wetting must take place. This means that a specific interaction must take place between liquid solder and the solid surface of the parts to be soldered. Solders can be classified as soft (melting point below 190 °C) and hard solders (melting point between 190 to 425 °C). The performance characteristics that are important include the melting temperature, the microstructure, IMC (intermetallic) formation and its inherent mechanical strength e.g. shear strength, fatigue behavior and creep behavior.

2.46.1 Melting Temperature

One of the fundamental performance characteristics of solder for industrial applications is melting temperature. For these applications, the melting temperature of the solder determines the maximum allowable temperature a product can be exposed to in service and the maximum processing temperature that devices and substrates can withstand during soldering. And, it is always desirable to have one same solidus and liquidus point that is called eutectic point. This eutectic point is desired in order to minimize the plastic region that is sensitive to mechanical movement or vibration that can lead to rejectable solder joint. The solidus and liquidus temperatures of various lead-free solders including Sn-Ag-Cu can be found in Table 2.3. Note that there are binary, ternaries and quaternaries alloys available.

2.46.2 Microstructure

The useful properties of materials are strongly dependent on their microstructure, which describes the grain structure and the combination of phases present in a material, as well as its defects, morphology and distribution. Generally, for a material of a given chemical composition, the microstructure is not constant and varies greatly, depending on processing and service conditions. In soldering assembly, the time-and-temperature-dependent soldering profile affects the microstructure of the solder joints, including the intermetallic layer thickness and the number of intermetallic phases present in the solder joint. The microstructure variation can drastically affect the fatigue life of the solder joint. Because operating temperature is a high homologous temperature for solder, the initial eutectic microstructure evolves over time. Homologous temperature is the ratio of operating temperature to melting temperature, e.g. 0.5 ($= 90^{\circ}\text{C} / 183^{\circ}\text{C}$). The lesser homologous temperature the better (Mulugeta and Guna, 1998).

2.6.32.4.3 Intermetallic Compounds (IMC)

Intermetallic compound (IMC) is defined as a distinguishable homogeneous phase having a relatively narrow range of compositions with simple stoichiometric proportion (Manko, 1979). The intermetallic compounds that are formed at the solder substrate interface continue to grow over time and increases with rising temperatures. This growth is a result of a solid-state reaction driven by an energy differential. The solder substrate reaction is exothermic, which means that the intermetallic compounds that are formed have a lower energy content than the reacting metal. Example IMC's are AuSn_4 , Cu_6Sn_5 , Cu_3Sn , Ni_3Sn_4 and etc.

Formatted: Bullets and Numbering

Each solder joint forms an intermetallic layer with each of the surfaces being joined together with the malleable tin-lead solder in between. The malleable nature of the tin-lead solder absorbs some thermal shock and mechanical stress, like a rubber bumper. This is ideal for the durable solder joint. But solder joints age. The intermetallic compound grows through time and with temperature. They often work together, but they can work independently. As time goes by, the intermetallic compound grows. Therefore, the tin-lead solder itself becomes a part of the intermetallic layer. Eventually, all that's left is intermetallic layer, which is both brittle and non-solderable. It is now susceptible to thermal and mechanical stress and can easily crack (Frear, 1974).

2.64.4 -4—Mechanical Properties

The mechanical properties of solder joints represent some of the most critical factors in soldering. The application of mechanical forces to a solid body causes the body to deform and may be even to fracture. Of special importance are the stresses and strains that are used to characterize the behavior of material under different types of mechanical loading.

The mechanical property of a solder joint defines the response of solder joints to imposed strains and stresses. The properties of major concern for solder applications are shear strength, ultimate tensile strength (UTS), ductility, creep and fatigue resistance.

Imposition of stresses and strains can be divided into three broad categories: time independent monotonic deformation, time-dependent monotonic deformation and cyclic deformation (Mulugeta and Guna, 1998).

2.6.4.12.4.4.1 Time-Independent Monotonic Deformation

Formatted: Bullets and Numbering

The deformations in this category are tensile and shear. When solid materials are subjected to small stresses they usually respond in an elastic fashion, i.e., the strain produced by the stress is reversible and the magnitude of the strain is proportional to the magnitude of the stress. This reversible deformation, where stress and strain is held constant, is called elastic deformation. With increased stress, the material starts to undergo plastic deformation. Once plastic deformation takes place, the material is deformed permanently and will not recover its original shape when the stress is removed.

2.6.4.22.4.4.2 Time Dependent Monotonic Deformation

Formatted: Bullets and Numbering

This deformation is commonly referred to as "creep," a measure of the time required for a material to fail when it is under a constant load at a constant temperature. Creep involves deformation mechanisms, such as grain boundary sliding, vacancy diffusion, etc., which require a thermal driven diffusion process. Therefore, creep deformation becomes critical only when the temperature exceeds half the absolute melting temperature of the

material. For most soldering alloys, operating temperature is well above half their absolute melting temperature. Consequently, for soldering, creep is considered the most important deformation mechanism.

2.6.4.32.4.4.3 Cyclic Deformation or Fatigue

Formatted: Bullets and Numbering

Fatigue, a measure of resistance to cyclic loading, can be isothermal or "thermal". Isothermal fatigue is where imposed cyclic displacement occurs at a constant temperature. Thermal fatigue, on the other hand, is a condition where cyclic displacement occurs due to a change in temperature, because of the joining of two materials with dissimilar thermal coefficients of expansion.

Fatigue in solder joints leads to crack initiation and crack propagation; the fatigue life of a solder joint is determined by the number of stress cycles it endures before a crack is initiated and propagates. Even when the cyclic stress is well below the yield stress of the material, fatigue failure can occur due to defects and irregularities in the microstructure that may serve as crack initiation sites.

Failure in solder alloys involves both fatigue and creep. For eutectic tin-lead solder, the failure mode in creep and in fatigue appears to be the same ([Mulugeta and Guna, 1998](#)). There is a scarcity of fatigue-resistance data for most of the Pb-free alloys.

2.75 — Why Gold Is Used ~~In Electronics Surface Coating~~?

The high electrical conductivity of gold, the low contact resistance and the good solderability, combined with constancy of these properties due to the chemical inertness of the metal, makes gold the ideal choice for many items of electrical and electronics hardware. Contacts, terminals, connectors, conductors, chaises, printed circuit board are routinely plated with gold or gold alloy. The good electrical properties combined with the excellent ductility of gold make it ideal for flexing or vibrating current carrying components. The resistance of gold to the formation of oxides, sulphides and other corrosion products suits it to application on safety devices, alarm and high reliability switches. Gold is used on waveguides and other RF conductors, grid wires and glass seal. Transistors make use of both pure and doped gold for eutectic bonding, resistance welding, formation of beam leads and making ohmic contacts to semiconductors.

2.8 — Gold in Semiconductors and Microelectronics

In spite of its major cost and consequent higher component cost, gold is still required because of its many desirable properties. Metal component piece parts are plated to protect the metal during the processing, testing and life of the device. Gold facilitates chip bonding (die attachment) and wire bonding due to its softness. It also provides tarnish, oxidation and corrosion resistance, good solderability, weldability and resistance to chemical etchants and low electrical contact resistance.

2.92.6 Thick Gold versus Thin Gold

Formatted: Bullets and Numbering

Thick gold is plated to 100 micro inches (2.5 μm) or more while thin gold is plated generally range from 20-60 micro inches (0.5-1.5 μm) or less (Frank, 1974). The justification for this classification rests historically in the attitude of the design engineer to porosity in gold plate. It takes 100-200 micro inches (2.5 to 5 μm) to have substantially pore-free gold. Pore-free gold is important in controlling contact reliability. Therefore, probably the most important application for thick gold deposits is on the edge contacts of printed circuit board and on the mating surfaces of their connector.

Thin gold deposits are specified when a good level of corrosion resistance is necessary, but where a pore-free deposit is not required. The bulks of connectors having gold plated contacts which serves general purpose application are plated with minimum 30-50 micro inches (0.75-1.25 μm) of gold, the underlaying being 30-150 micro inches (0.75 –3.75 μm) of copper or nickel. Nickel is more popular and normally used as a diffusion barrier between copper /gold with 2 μm as a safe specification (Don, 1998).

In more recent findings, as soldering to gold deposits of 30-100 micro inches (0.75- 2.5 μm) resulted in some commonly associated problem of “embrittlement”, gold thickness becomes ultimately important and critical. For tight hermetic requirement product

however example in optoelectronic industry, gold on fiber metallization cannot be too thin ($< 1\ \mu\text{m}$) because of porosity and short shelf life. The Au dissolution and AuSn_4 IMC formation will embrittle the joint and result in losing hermeticity (Jin, 2003). With the emergence of plating process that can produce denser, less porous deposits, a thinner gold deposit of 5 - 15 micro inches ($0.125\text{-}0.375\ \mu\text{m}$) is becoming popular now for most application (Ronald, 1998).

2.102.7 Gold-Solder Embrittlement Issue

Formatted: Bullets and Numbering

It is well known that soldered connection made to gold plated surfaces can lead to unreliable or mechanically weak bond, due to the rapid formation of intermetallic compound during soldering (Cotts(1), 1999). A very careful control of the gold thickness and the soldering conditions is needed in order to have a satisfactorily low failure incidence. It is generally reported that there is apparently lower mechanical strength of soldered connections on gold plating when gold content is 3.5-5.0 wt% (Frank, 1974). Gold has the highest dissolution rate in solder compared to metals like Ag, Cu, Pd and Ni (Refer to Figure 2.1) and this had led to high formation of intermetallic (IMC) formation. Figure 2.2(a) shows when gold amount increases to 8-10 wt%, ductility drop to almost zero and he also found simultaneous increase in hardness (Figure 2.2(b)). This would normally expect to lead to increase in tensile strength, however strengthening was counteracted by simultaneous loss in ductility. The study using impact test as in Figure 2.2(c) shows that 4% gold in 63-37 tin-lead solder causes no deleterious effects, a 5% addition results in drop in impact strength from 80 to about 25 in-lb. Izod Impact is a single point test that measures a materials resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic

energy needed to initiate fracture and continue the fracture until the specimen is broken (Frank, 1974).

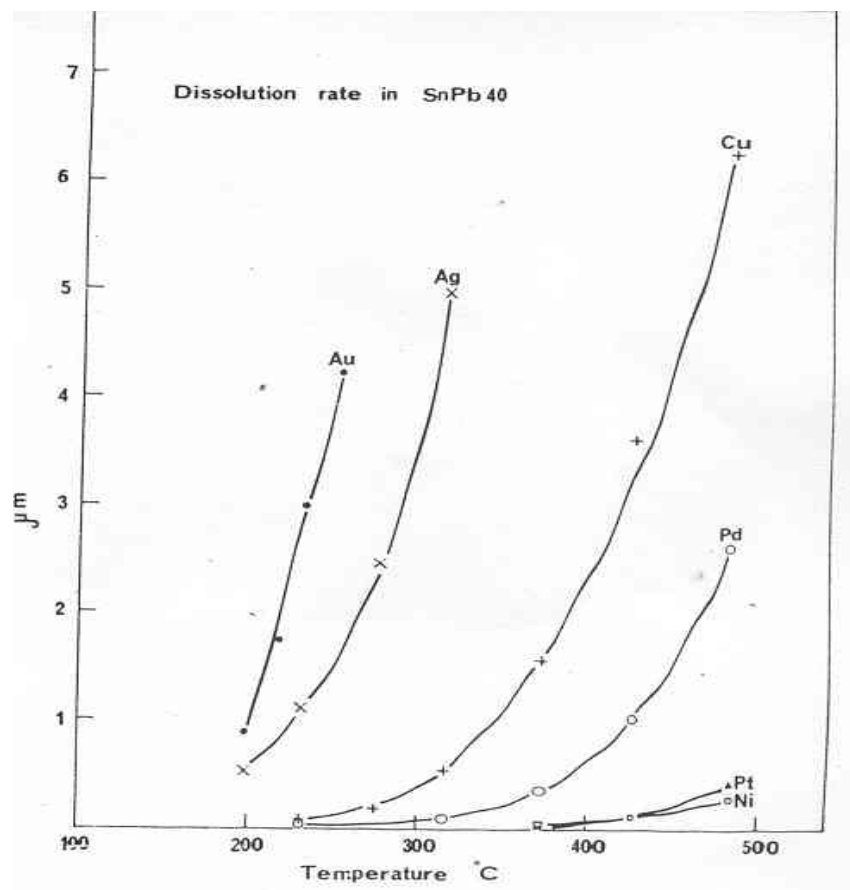


Figure 2.1 Dissolution rates at various temperatures for a number of metals in 60%Sn 40% Pb solder. [Frank, 1974]

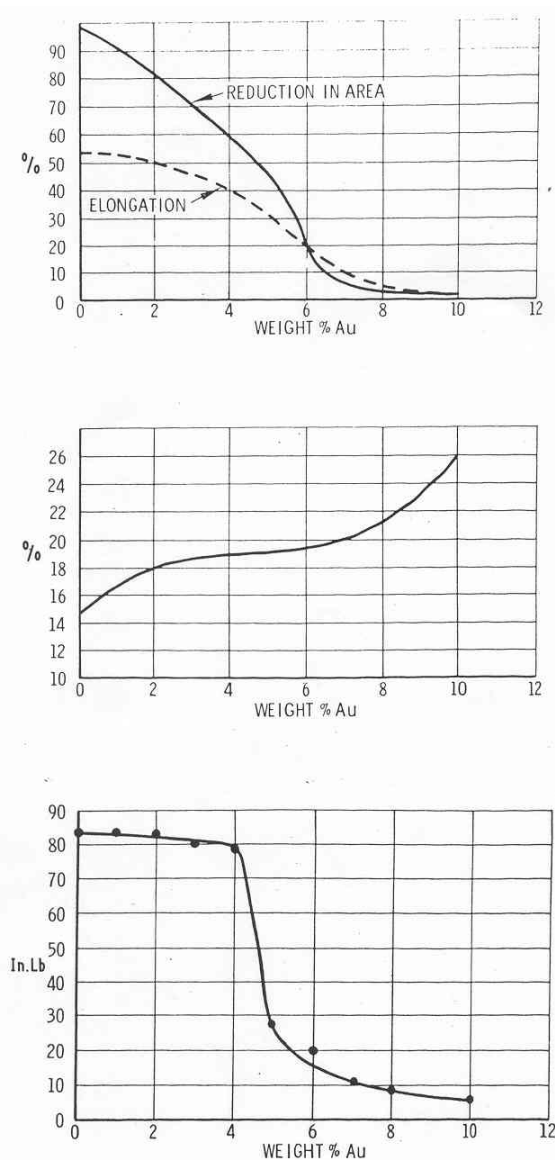


Figure 2.2 (a) *Top*: Influence of Gold content in 63%tin-37% lead solder on tensile strength ductility.

(b) *Middle*: Diamond hardness of 63%tin-37% lead solder for various gold contents.

(c) *Bottom*: Effect on impact strength of 63%tin-37% lead solder of increasing concentration of gold. [Frank, 1974]